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## Overview

This report describes the progress and accomplishments for the period September 25, 2004 – June 30, 2008 for the MURI grant “Accurate Theoretical Predictions of the Properties of Energetic Materials” (No. DAAD19-02-1-0176). This is a multi-university, comprehensive theoretical/computational research program to develop, validate, benchmark, and apply methods and models that will provide predictive capabilities for energetic materials. The thrust of the work is the development of atomic-level models and *ab initio* quantum chemistry methods that are generally applicable to the chemical decomposition of condensed-phase energetic materials under extreme conditions.

The approaches include quantum mechanics, molecular modeling, Monte Carlo, and molecular dynamics to yield state-of-the-art methods specifically designed for and tailored to target DoD energetic materials research needs. The following is a list of the principal investigators, universities, and topics that make up the overall MURI project:

- **University of Missouri - Columbia**; Professor John E. Adams (PI); *Gas-liquid heat transfer*
- **University of Maryland**; Professor Herman L. Ammon (PI); *Crystal models*
- **University of Florida**; Professor Rodney J. Bartlett (PI); *Quantum Chemistry*
- **North Carolina State University**; Professor Donald W. Brenner (PI); *Reaction potentials*
- **University of Illinois**; Professors David Ceperley and Richard Martin (PIs); *Solid-state quantum mechanics*
- **University of Missouri - Columbia**; Professor Donald L. Thompson (PI); *Reaction dynamics and simulations*
- **University of Minnesota**; Professors Donald G. Truhlar and Christopher J. Cramer (PIs); *Solvation models*

The focus of the project is on developing accurate methods for simulating physical and chemical processes in condensed-phase energetic materials. The MURI team is working closely with researchers at DoD labs, who are contributing to the theoretical efforts, providing data for testing of the models, or aiding in the transition of the methods, models, and results to DoD applications.

The major goals of the project are:

- Models that describe phase transitions and chemical reactions in condensed materials.
- *Ab initio* predictions of structures and properties of solids at high temperatures and pressures.
- Methods to predict mechanical properties and physical changes in condensed phases, including thermodynamic quantities, phase diagrams, vibrational frequencies, tensile strength, stress/strain relations, and densities.
- Simulation methods to predict chemical decomposition in condensed phases, particularly ignition and sensitivity in response to heating and shocking.
- Methods for predicting temperatures of the condensed phases and flames resulting from physical and chemical changes, including a predictive model for the “heat feedback” from the flame to burning surface.
- Methods for predicting solvation and separation for energetic materials in supercritical fluids.

The following are descriptions of the component efforts that make up the overall project.

## Structure and Solid-State Density Prediction

**Herman L. Ammon** (Department of Chemistry and Biochemistry, University of Maryland)

The discovery of new energetic materials can be facilitated, accelerated and made more cost effective with the use of computer modeling and simulations for the identification of compounds that have significant advantages over materials currently in use. The quantitative estimation of key parameters can be used to screen potential energetic candidates and permit the selection of only the most promising substances for laboratory synthesis and development.

The most significant properties or characteristics of a high performance energetic material are the molecular structure and elemental composition, and solid-state heat of formation, density and microstructure (3-D structure with various dislocations and defects). Our primary goals are the development of procedures for the prediction of the crystal structures, accurate densities and heats of formation of energetic materials, and to investigate the relationships between crystal structure/microstructure and sensitivity, compressibility, polymorphism and crystal shape.

A three step model-packing-refinement procedure to predict the crystal structure of a material from an initial molecular model has been developed and extended to the major types of energetics, bonding patterns and symmetries. The MOLPAK (MOlecular PAcKing) procedure/program takes into account molecular structure and conformation, probable crystal packing arrangements and efficiency. Hypothetical structures are assembled based on the structure of a "search probe" (molecular model) and molecular coordination information obtained from analyses of more than a thousand experimental crystal structures. The coordination information, for the major triclinic to orthorhombic space groups with  $Z'$  of one-half or one, covers approximately 94% of the known crystal structures of C-H-N-O-F-containing materials.

MOLPAK utilizes the repulsion part of a 6-12 interatomic potential to position the search probe elements in a hypothetical crystal lattice. The repulsion-only terms dramatically accelerate the positioning calculations because the interatomic energy summation between a molecule and its neighbors is terminated when the energy reaches a pre-determined threshold.

The rigid search probe approach used in the MOLPAK procedure to create hypothetical crystal structures is adequate if crystal forces do not appreciably alter the molecular conformation from that in an isolated molecule. A procedure (ROTPAK, the ROTational PAcKing program) has been developed to allow conformational flexibility concomitant with crystal packing. The addition of flexibility substantially complicates the packing process and requires a fine-tuned potential to balance the intra and intermolecular contributions to the overall energy. A preliminary example of the potential of ROTPAK is found in packing calculations for 1,3-dinitrocubane. The experimental, MOLPAK-predicted and ROTPAK-predicted densities are 1.647, 1.620 and 1.646 g cm<sup>-3</sup>, respectively, and the C-NO<sub>2</sub> twist angles from ROTPAK are within a few degrees of the X-ray values.

The third step in the overall model-packing-refinement crystal structure determination is refinement of the best of the MOLPAK/ROTPAK structures by optimization the unit cell parameters and position and orientation of the search probe. Intramolecular adjustments also are necessary for ROTPAK calculations. The refinement entails minimization of the crystal lattice energy with either the WMIN/PMIN or DMAREL/DMACRYS lattice energy and refinement

procedures/programs. The WMIN/PMIN intermolecular potential contains a simple Coulombic term and standard 6-exp terms for attraction and repulsion;  $e_i$  is a point charge on atom  $i$  from electrostatic potential calculations (6-31g\* basis set),  $r_{ij}$  is the distance between atoms  $i$  and  $j$  and  $A$ ,  $B$  and  $C$  terms are empirical coefficients. The DMAREL/DMACRYS potential is similar, but with a distributed multipole electrostatic term (6-31g\*\* basis set) in place of the WMIN/PMIN monopole.

$$E_{WMIN} = \sum(j \neq i) e_i e_j / r_{ij} - (A_i A_j) / r_{ij}^6 + (B_i B_j) \exp[-(C_i + C_j) r_{ij}]$$

The A-C coefficients in both potentials are obtained by fitting calculated to experimental structures, crystal densities and available heats of sublimation. A major effort was required for parameterization of the various atom functionality. There are, for example, different coefficients for the nitrogens in C-NO<sub>2</sub>, N-NO<sub>2</sub>, N-NO<sub>2</sub> and ordinary amines. The necessary program infrastructure for automatic coefficient optimization (simplex followed by least squares) is in place and requires effort primarily in the set-up of input data sets and experimental data quality evaluations. The limited experimental heat of sublimation data (related to lattice energies) possibly can be supplemented with *ab initio* energies with appropriate corrections. Additionally, the solid-state heats of formation can be obtained by the appropriate combination of the WMIN/PMIN/DMAREL/DMACRYS lattice energies and molecular heats of formation from *ab initio* calculations. Additionally, these procedures and potentials can be used to investigate/predict polymorphism and crystal habits.

Sensitivity, the ease with which a material undergoes a violent reaction or detonation, is defined in relation to particular tests or stimuli such as impact, shock, friction, thermal and electrostatic sources of energy. A number of molecular structure-sensitivity relationships have been found over the years and good correlations observed within families of energetic materials. Sensitivity is perhaps the most complicated and least well understood of the various derivative properties of energetic materials. Areas that can be explored with structure predictions for unknown materials: (1) Density of states relationship of Kunz which requires the crystal structure and appropriate *ab initio* crystal lattice calculations. (2) Possible relationships between impact sensitivity and bond strength plus lattice energy. The basic idea is that impact has an important frictional or heat component that initially causes disruption (melting or deformation) of the crystal lattice followed by homolytic cleavage of the weakest bond in the molecule leading to detonation. Lattice energies are available from WMIN/PMIN/DMAREL/DMACRYS calculations and bond energies (e.g., C-NO<sub>2</sub>, N-NO<sub>2</sub>, O-NO<sub>2</sub>) from *ab initio* calculations of the energies of the appropriate framework and nitro group radicals. (3) A correlation between the impact sensitivity and hydrostatic compressibility (from molecular dynamics calculations) for a variety of energetics has been observed. (4) The lattice potentials developed can be utilized to explore the relationship between crystal orientation and detonation. In PETN, for example, the orientation to shock initiation and detonation is consistent with steric hindrance to shear at the molecular/crystal level.

Details of the MOLPAK, PMIN, ROTPAK and volume additivity codes follow.

**MOLPAK-1.** The computer code typically used to generate hypothetical packing arrangements is termed here MOLPAK-1, to distinguish it from a new generation code under development termed MOLPAK-2. MOLPAK generates hypothetical crystal packing motifs that mimic the experimental coordination geometry information determined from the analysis of 1000's of C-H-N-O-F crystal structures in the triclinic, monoclinic and orthorhombic space

groups. Analysis of the three-dimensional crystal packing arrangements, with the MOLCON/MOLPAN (molecular connectivity/molecular packing analysis) codes, revealed a relatively small number of common coordination patterns and this information was used to construct routines to handle 54 distinct patterns. The patterns are based on a coordination number of 14, the number of molecules in van der Waals contact with a central molecule. We typically use only 31 of the 54 geometries which cover the majority of cases for energetic materials. Additionally, MOLPAK-1 handles molecules with  $C_i$ ,  $C_2$  and  $C_s$  point group symmetries in which the molecule is coincident with appropriate unit cell symmetry.  $\beta$ -HMX, for example, has  $C_i$  point group symmetry and the molecule occupies a center of symmetry in the  $P2_1/c$  space group.

In the construction of hypothetical crystal structures for each of the coordination geometries, MOLPAK typically rotates the model of interest (search probe) about three Eulerian axes by  $180^\circ$  in  $10^\circ$  steps for a total of 6,859 orientations, each of which is used to generate a possible crystal structure. The number is 50,653 for a  $5^\circ$  step search. MOLPAK has been expanded to save up to 60,000 hypothetical structures and to pass up to 5,000 of the highest density for subsequent lattice optimization. Generally, after eliminating identical solutions and averaging similar adjacent solutions, the number remaining for optimization is on the order of 1-2,000.

**PMIN.** Each of the MOLPAK-generated structures is refined by lattice energy minimization to optimize the unit cell parameters, orientation and position of the search probe. The work-horse refinement code WMIN, developed in the late 70's, has been replaced by a simpler, cleaner and easier to understand code named PMIN. The major features are (a) modern fortran 90/95; (b) step and least-squares optimization; (c) facile multiple molecule/fragment refinement, such as cation-anion complexes; (d) both lattice and molecular conformation refinement; (e) ability to easily use individual cross-term potential coefficients. Such as for H- bonding; (f) potential energies can be calculated either by Ewald or direct summations or a combination of the two; (g) user defined potentials are easily implemented.

**ROTPAK.** Conformational changes concomitant with the crystallization process can occur in a number of flexible molecules. This is evident if one compares the structure of an optimized model or vapor phase conformation (no-neighbor conformation) with that found in the solid state. The flexibility inherent in the eight-membered HMX gives rise to crystals in which the molecular point group symmetries are  $C_i$  and  $C_2$ . The ROTPAK code, similar to MOLPAK, was developed to permit limited conformational changes to accompany the typical packing process. Subroutines have been added to permit bond rotation (e.g.  $C-NO_2$ ), out-of-plane bending (e.g.  $C_2N-NO_2$ ) and bond angle variations. The packing process requires an appropriate mixture of the individual inter and intramolecular energies. The latter are currently evaluated with external calls to Gaussian-03 to obtain, for example, semi-empirical energies such PM3 or *ab initio* b3lyp/6-31g\* energies. An important part of this procedure is the lattice plus conformational refinement by total energy minimization. Conformational refinement additions have been added to the step search portion of PMIN and changes to the least-squares routines are planned.

The basic packing procedures in MOLPAK and ROTPAK differ, although both utilize the same coordination geometry information for packing construction. MOLPAK has a repulsion-only potential and molecules are docked until a pre-determined repulsion threshold is met. This accelerates packing because calculation of the total repulsion energy between molecules can be terminated as soon as the threshold is achieved, the distance is then increased and the calculation repeated. In ROTPAK, however, the intermolecular energy between two (or more) molecules is

calculated with the same q-6-exp interatomic potential used in PMIN and distances are adjusted to a minimum energy. The results from MOLPAK and non-flexible ROTPAK calculations are similar, in most cases, and generally the same after PMIN refinement.

**DMAREL** (distributed multipole analysis relaxation). The program, an alternative to PMIN for lattice refinements, uses a distributed multipole electrostatic term in place of single atom-centered charges. The set-ups for the calculations are complicated and somewhat clumsy, despite several automatic procedures we have introduced, and the refinements are 4-5 times slower than with PMIN. Generally, we have preferred the easier and faster codes but recently have returned to the superior results typically provided by DMAREL. DMAREL was developed at University College London and is being replaced by DMACRYS.

**VOLUME ADDITIVITY.** Appropriate atom and group volumes can be summed to estimate an effective solid-state molecular volume for a substance, which in combination with the molecular mass provides an estimate of the crystal density. With crystal structure data from the Cambridge Structural Database, four new additivity data bases have been determined to provide atom and functional group volumes or densities for the calculation of solid state densities of single organic compounds, organic salts and multi-fragment materials with the elements H, C, B, N, O, F, P, S, Cl, Br and I. Linear and nonlinear volumes and linear densities were determined for 108 pre-defined atoms/functional groups from  $\sim 41,000$  crystal structure data. In separate calculations, the use of atom\_codes, which do not require a beforehand atom or functional group specification, allowed the atoms and their connections to automatically define the types of atoms present in a molecule. This approach, applied to both single molecule and multiple species unit cells (e.g.,  $Z' > 1$ , hydrates, cation + anion), lead to 2,805 atom\_codes from  $\sim 48,000$  structures. With 1,027 crystal structure data not used in the initial parameterizations and the atom\_code volume parameters, the average percent difference between the observed and calculated densities was 2.3%. Similarly, 864 new structures with the 108 atom/group parameters gave a 2.0% average volume difference with the linear volume parameters. This work has been published in Propellants, Explosives, Pyrotechnics.

**MOLPAK-2.** The present MOLPAK-1 code is based on constructing hypothetical crystal packing arrangements to mimic experimental crystal structure motifs. MOLPAK-1 has certain limitations, not the least of which is the inability to handle new crystal symmetries and space groups that previously have not been coded. MOLPAK-2 is designed to determine the most likely packing arrangement from little more than the structure of the search probe and crystal symmetry information, such as the space group and symmetry operations. The starting point for MOLPAK-2 involves finding low energy pairs of molecules that are related by unit cell translations, inversion centers, two-fold screw axes, mirror glide planes and other possible symmetries dictated by the unit cell symmetry. These motifs of molecules are expanded to possible unit cells. Unlikely solutions are culled by the elimination of close intermolecular contact structures and accepting only those with densities within 0.1 g/cc of a pre-estimated, volume additivity values. Complete lattice energy calculations with PMIN are used to select the most probable solutions.

The codes for the triclinic space groups P1 and P-1 and the monoclinic P2<sub>1</sub> are complete and have been tested. Work is progressing on the considerably more complicated (and potentially important) P2<sub>1</sub>/c. A possible enhancement of the basic MOLPAK-2 concept is the simultaneous use of information from two types of pairs.

## First Principles Simulations of Energetic Materials

**David Ceperley and Richard Martin** (Department of Physics, University of Illinois, Urbana-Champaign)

A large part of our effort has gone into developing the quantum Monte Carlo code QMCPACK to allow more efficient QMC calculations of energetic materials. The code has been publicly released. A presentation of Monte Carlo methods and the use of the code was made at the Army Research Lab in July, 2007.

In our developments of new methods, we extended QMC methods to compute energy differences. This is an important general problem in QMC and we are developing methods for an efficient and accurate determination of dissociation energies, reaction barriers and the entire energy curve for the bond-dissociation, and weak intermolecular interactions in molecular crystal and van der Waals complexes.

These problems are especially important in energetic materials and QMC will allow us to compute such properties for as big complexes as the benzene and RDX dimers. Our approach based upon the reptation Monte Carlo and is being tested on dissociation of diatomic molecules.

We have completed work on a new method to determine the finite size error on the energy for quantum systems in periodic boundary conditions. This is important for work on condensed phases and we have tested the method on the uniform electron gas, solid silicon and solid nitrogen. The results of this work are published in *Phys. Rev. Letters*.

We are developing coupled electronic-ionic Monte Carlo methods for applications beyond hydrogen. Preliminary testing for systems of water molecules is in progress. This is a long range project that has the potential to provide a new level of accuracy and reliability of predictions for materials under extreme conditions.

We have initiated work to implement and apply recently-developed optimization methods in Variational Monte Carlo (VMC) which the accuracy and allow atomic geometries can be optimized simultaneously with minimizing the parameters in the electronic wave function. The main goal is to treat using methods that have recently been applied to benzene and benzene pairs. The first application is to benchmark calculations for a system like H<sub>2</sub> adsorbed on benzene; a difficult case with very binding energy.

## *Ab initio* Predictions for Potential Energy Surfaces for Chemical Reactions

**Andrew G. Taube, Josh McClellan, and Rodney J. Bartlett** (University of Florida, Quantum Theory Project, Gainesville, FL 32611-8435)

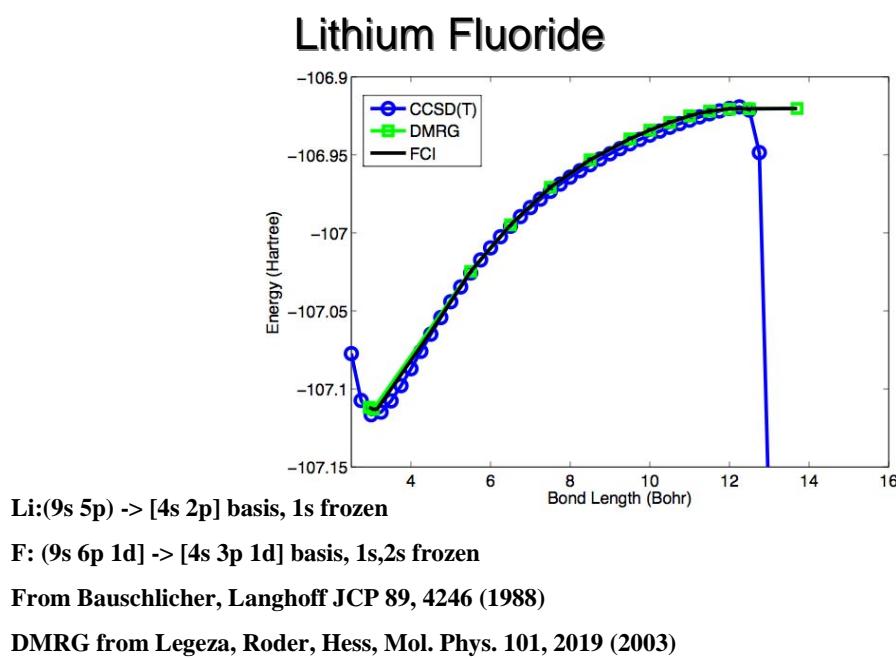
### Decomposition Pathways of Nitroethane

The 2006 report summarized this extensive work, so that will not be repeated here. Suffice it to say, that the major new development was the introduction of frozen natural orbitals (NO) into coupled-cluster (CC) theory, which have the effect of reducing the computational dependence of the CC calculation by about an order of magnitude with no loss in accuracy. This required that entirely new theory for the analytical derivatives (forces) of NO based CC be developed and implemented into ACES II. Using this new capability, a very thorough, predictive study of the decomposition and rearrangements of the prototype energetic nitroethane molecule was presented with state-of-the-art CC methods. The discrepancies with the results from DFT calculations were considerable, suggesting that DFT, as used for these systems, is not a reliable

tool to understand the comparative importance of the various reaction paths. The lowest path in the case of nitroethane was found to be the HONO elimination. This paper is now published in the *J. Chemical Physics*.

### ACCSD(T): The new “gold-standard”?

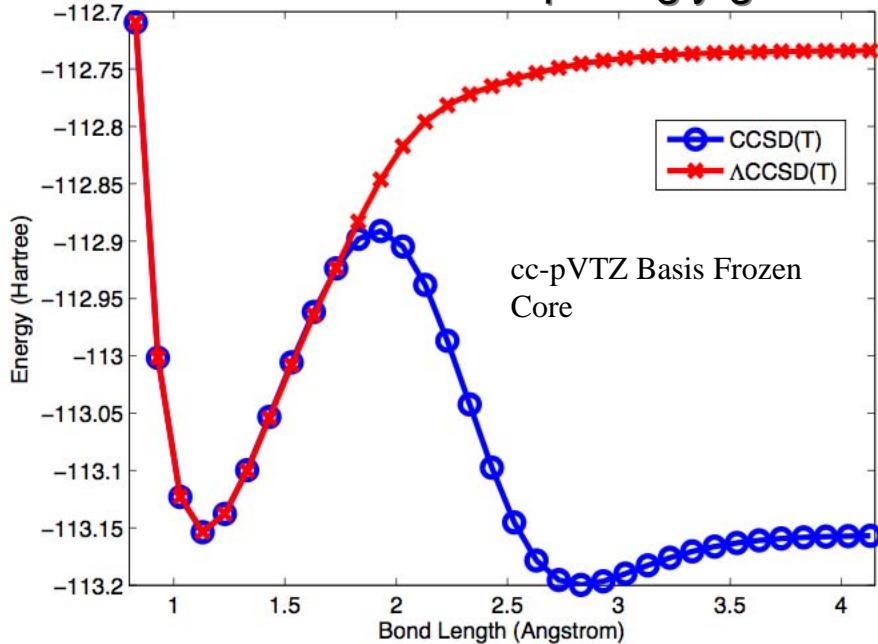
For some years, the gold standard for quantum chemistry has been the CCSD(T) method, as it is fairly widely applicable to moderate sized molecules. However, the (T) part means that coupled-cluster single and double excitations (CCSD) is augmented by a non-iterative, perturbative, triples correction. It is well-known in the field, that once bonds start to be broken, as in a transition state (TS), that such perturbative corrections can fail dramatically, particularly when using a spin-adapted RHF reference function. An illustration is shown below for breaking the LiF bond.



What should be observed from this figure is that at larger internuclear separation, that CCSD(T) falls precipitously off the correct curve, here defined by the full CI. Note, however, that once the new ACCSD(T) method is applied to this problem, that a good curve is obtained all the way to the dissociation limit.

This is not an isolated situation, as this can be observed in nearly all bond breaking as illustrated for the triply bonded CO molecule.

## Carbon Monoxide: Surprisingly good



The failure of CCSD(T) as the bond length is extended beyond its equilibrium geometry suggests that for transition states that are farther from the molecule's equilibrium geometry, it will be difficult to be definitive for TS geometries and their associated activation barriers. However, as we have already seen in the nitroethane example, DFT cannot be expected to sort out competitive paths correctly, so there is a need for the best CC methods to be applicable to the problem.

The ΛCCSD(T) method is still perturbative, like CCSD(T), which gives it its high applicability; but unlike that method, benefits from the use of a left-hand eigenvector,  $\Lambda$ , that is determined prior to imposing the (T) correction. By so doing, many of the effects of the perturbation approximation are removed, providing a much more stable treatment of molecular geometries away from equilibrium. A case in point is the ‘triple-whammy’ fragmentation of RDX to three equivalent units. This has been supported by Yuan Lee’s molecular beam experiments, but is disputed by most explosives experts who anticipate that there is a direct bond fission of the nitramine bond. Some of the issues include the comparative relevance of the unimolecular dissociation path versus that observed in condensed phases, where bimolecular mechanisms might predominate; and the comparative entropies along the different unimolecular paths. This feature points to a need to obtain the more relevant free energy paths, at the cost of doing a vibrational analysis for the zero-point and entropy at every relevant geometry along the dissociation path. We are currently trying to help resolve this question by using the ΛCCSD(T) method for those TS’s.

As in all *ab initio* studies that require searching potential energy surfaces to locate TS’s and equilibrium geometries, the development of analytically computed gradients is requisite. So much of our time was necessarily devoted to this development, that is particularly difficult for ΛCCSD(T). However, this has now been done successfully and we have applied the theory to a variety of TS studies. This work has been published in two papers in the J. Chemical Physics.

### **Adaptive *Ab Initio***

The basic reason for developing the adapted *ab initio* theory (AAT), is to offer an alternative to the current semi-empirical quantum chemical approaches for very large scale, quantum mechanically based forces for classical molecular dynamics (MD) simulations of condensed phase explosives. The more sophisticated QM methods, like CC theory, MBPT, and even DFT, cannot be applied on a rapid enough time scale to tie naturally with classical molecular dynamics methods. Yet we require this capability to allow for bonds to be broken in detonation while we use MD to observe the time development of the species. The alternative today, is to employ classical force fields for the MD step, but such approaches have to compromise on the details of the reactions and when applicable, on the spectroscopic signatures that might be observed for the phenomena. Hence, only semi-empirical theory like MNDO, AM1, PM3, and their many variants can be used today. Yet all these are easily shown to be unable to correctly describe the potential energy surfaces required for bond breaking.

The philosophy of AAT is to use rigorous, *ab initio* theory based upon a combination of wavefunction and density functional theory as the foundation for a new, very efficient QM evaluation of energies and structures for  $\sim$ 1000 atoms. All approximations introduced---of which none are semi-empirical---are assessed compared to accurate correlated theory, to determine their viability. Yet at the same time, these approximations are made with the objective of routinely treating  $\sim$ 1000 atoms. Currently, this approach is being put into ACES III, the new parallel version of ACES, to make very large-scale applications and to further assess the strengths and weaknesses of AAT, to identify how it can be improved.

### **Plans For The Future**

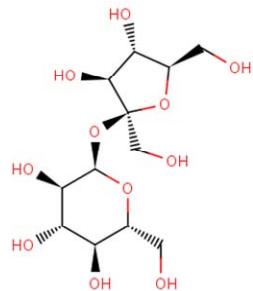
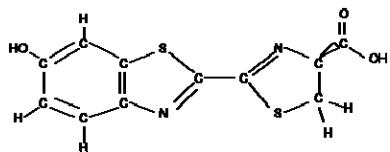
We have now shown that ACES III scales at 100% efficiency up to 512 processors (see below), which is all we have been able to access at the DoD HPCMO installations. In the transition to petascale applications, of which DoD is a major player, this has to be fixed for future developments. Only with routine access to  $>$ 1000 processors for relatively short periods of time for debugging purposes, like 15 minutes, can the software be adequately developed to begin to explore even the terascale on the way to the petascale.

With the development of ACES III, which has been written from scratch even to writing an entirely new integral and integral derivative program; we are poised to make some of the definitive computations of great interest to ARO. An example is the RDX molecule's unimolecular dissociation paths, where with ACES III's analytical gradient methods, this path can be studied in depth. Even the paths for the dimer of RDX as it falls apart can be described. For rigid RDX molecules, MANY points have been done by Szalewicz and Rice to fit a force field, which is already a monstrous calculation, but the real dissociation paths demand relaxing its geometry in all possible ways. Such a study has been well beyond the capability of nay prior CC work, but can now be envisioned with ACES III and adequate computer resources.

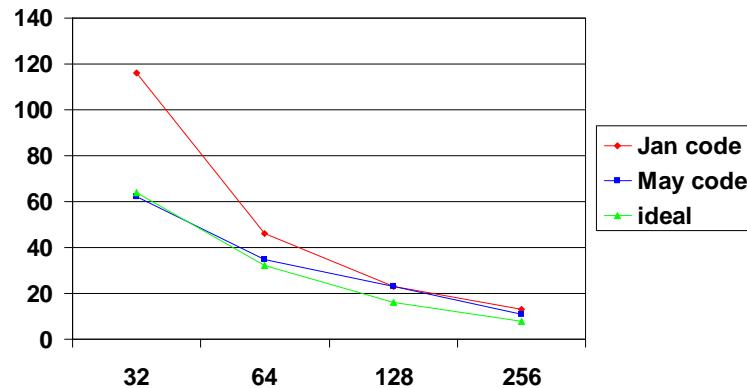
Furthermore, ACES III also offers excited states with the equation-of-motion (EOM-CC) method, another unique feature in such a parallel CC program (see below for scaling).

## CCSD(*T*)

- Luciferin( $C_{11}H_8O_3S_2N_2$ )
- RHF
- $C_1$  symmetry
- Basis = aug-cc-pvdz (494 bf)
- $N^{corr}_{occ} = 46$
- Sucrose ( $C_{12}H_{22}O_{11}$ )
- RHF
- $C_1$  symmetry
- Basis = 6-311G\*\* (546 bf)
- =68



*Luciferin CCSD scaling  
min per iter; 12 iterations; two versions;*



## *Luciferin CCSD(T)*

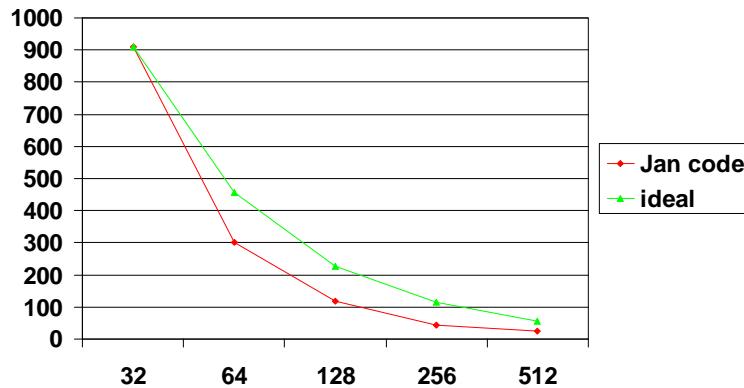
- CCSD on 128 processors
  - One iteration: 23 min
  - Total 12 iterations: 275 min
- (T)
  - Hardest 8 occupied orbitals: 420 min on 128 processors
  - Total 48 correlated orbitals: 420 min on 768 processors

34

ACES III

Jul 17,  
08

## *Sucrose CCSD scaling min per iteration*



35

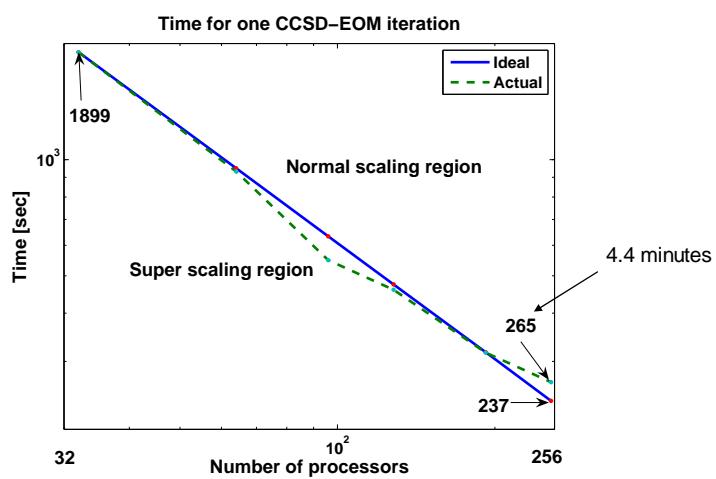
ACES III

## *Succrose CCSD super linear scaling*

- CCSD iteration
  - 32 processors 909 min
  - 512 processors 24 min, ideal: 57 min

36

ACES III



## **Progress toward the Development of Transferable Bond Order Potentials for CHNO**

**Donald W. Brenner** (North Carolina State University)

We have developed analytic potential functions for CHNO clusters, solids, and molecular materials that have a transferable functional form that is independent of molecular structure. The bonding formalism is based on a second-moment approximation in which a bond-order whose value is proportional to the inverse square root of local coordination is coupled to an attractive pair term that represents bonding from valence electrons. Together with a pair-additive, largely repulsive term, this functional form is capable of reproducing Pauling bond length/bond order/bond energy relations over a wide range of coordinations, while allowing bond breaking and forming with appropriate effective atomic rehybridization in a computationally efficient manner. These functions represent an important bridge between first principles methods and large-scale atomic simulations.

Determination of functional forms and parameter fitting for transferable pair terms, bond order and screening functions, as well as a novel molecular topology function were all completed and incorporated into molecular dynamics codes at both NC State and the ARL. Part of the fitting process for oxygen made extensive use of first principles results generated within the MURI team. Extensive testing of the potential, including comparison to additional first principles results, has revealed that it is robust with respect to reactive dynamics and the production of intermediate compounds that were not an explicit part of the fitting data base.

While the development of the functional form and the delivery of a working code to the ARL was successful, testing has revealed the functional form and its implementation to be too slow for many of the uses targeted by ARL researchers. Over the last year we have worked to make the potential and associated code more computationally efficient without loss of accuracy or transferability. As an example, the screening function in the topology expression was replaced with a distance-dependent function, and a new implementation of the screening function that takes advantage of inherent properties of the function was accomplished. More efficient neighbor indexing was also implemented within our codes. These changes have sped the code up over a factor of 60, which broadens its use for DoD and related applications.

## **Flame-Surface Energy Feedback**

**John E. Adams** (University of Missouri – Columbia)

Over the period of this project, we completed the characterization of the basic features of energy feedback from hot combustion products to the liquid layer atop a deflagrating propellant in simulations of both prototypical model systems and actual energetic species. In all the systems investigated, we have found that the net transfer of energy to the liquid surface is captured in a simple kinematic model, the general form of which was devised originally by Baule to describe gas scattering from a solid surface. This model previously was identified by Nathanson as providing a useful depiction of his experimental measurements of energy transfer at a liquid interface, but we have been able to test the model over a range of conditions wider than that accessible in the experiments and to verify in more detail its general utility in describing the net flow of energy back to the liquid surface. We also have assessed the role played by the internal vibrational degrees of freedom of a molecular liquid in collisional energy

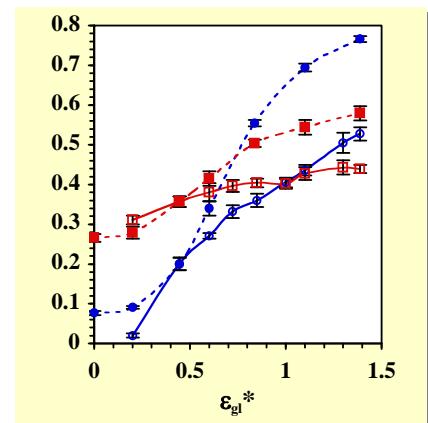
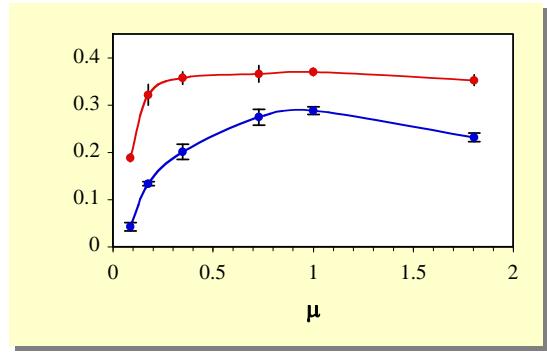
transfer and have determined the extent to which the initial translational energy of an impinging gas molecule is deposited in rotation of that species. The investigations yielding these generalizations are described in more detail below.

Our simulation methodology was calibrated in studies of energy exchange in a simple, prototypical atomic system (Lennard-Jones interactions). Having first equilibrated a sample of the neat liquid under conditions of constant density and temperature, we expanded the simulation cell along one dimension thereby creating two interfaces. (The potential energy function cutoffs are such that the two interfaces do not “see” one another.) The resulting system is again equilibrated, and a series of temporally well-spaced system snapshots is collected for use in setting the initial conditions of the subsequent microcanonical trajectories from which final energy spectra and trapping probabilities are extracted.

For this system, the significant trapping probabilities obtained attest to the high efficiency of energy transfer for a wide range of projectile/target combinations. The figure here corresponds to results generated using a high initial incident energy, but even here we find that a sizeable fraction of the incident species lose sufficient energy (on average the energy loss is over 70%; the thermal accommodation coefficient is, roughly, 0.8) that they are (essentially) equilibrated with the surface. Of particular importance in these results, though, is the dependence on  $\mu$ , the ratio of the incident particle mass to the surface atom mass, with the maximum in the trapping probability appearing when the particles are equal in mass and with a suppression of the sensitivity of the trapping to  $\mu$  at higher surface temperatures (the upper set of points).

One also expects that the probability of becoming trapped to depend on the strength of the attractive interaction between the incident and surface species. Indeed, that expectation was borne out in the calculations summarized in the next figure in which we varied the interaction well depth (either by scaling the full interaction energy—the solid lines—or by modifying only the attractive component of that energy, thereby retaining the full short-range repulsive component—the dashed lines). It is not surprising here that a deeper attractive well leads to increased trapping or that more energy is transferred (and thus more trapping occurs) when the full short-range repulsive interaction is included in the potential, but it is again interesting to note the strong surface temperature dependence of the trapping probability. Trapping on the cooler surface, while less probable for small attractive well depths, actually becomes more probable than trapping at the warmer surface when the well depth is relatively large. Again, we find a notable suppression of the sensitivity of the trapping (and hence of the energy transfer) to the initial collision conditions when the surface temperature is increased.

The real contribution to our understanding of energy feedback in flames comes, however, from recognition that these results evince a quite simple model of the underlying particle dynamics, one that derives from the work of Baule dealing with gas-solid surface energy

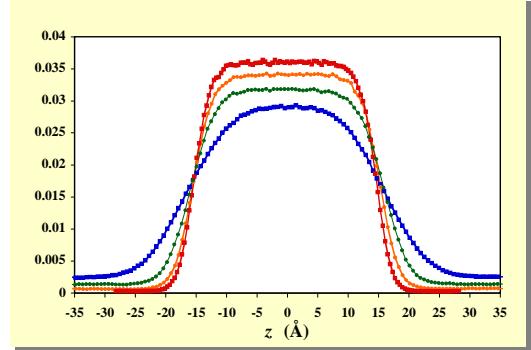


transfer. If the incident atom is assumed to be normally incident with kinetic energy  $E_i$  on the final atom in a one-dimensional harmonic atomic chain, then one can show that the fractional energy transfer is given by the expression

$$\frac{\Delta E}{E_i} = \frac{4\mu}{(1+\mu)^2} \cdot \frac{1}{2} \left[ -\cos \chi \left( 1 - \mu^2 \sin^2 \chi \right)^{1/2} + \mu \sin^2 \chi \right] \left[ 1 + (V - 2RT_\ell)/E_i \right],$$

where  $\mu$  again is the incident/target atomic mass ratio,  $\chi$  is a deflection angle (which enters because the line-of-centers of the initial collision may not coincide with the surface normal),  $V$  is the depth of the gas-surface interaction potential (assumed to be a square well), and  $T_\ell$  is the temperature of the bulk liquid. This same expression was used by Nathanson in interpreting the general trends in his experimental studies, but by extending the range of system parameters studied beyond those currently tractable by experiment, we can show that this estimate of the energy transfer has broad applicability to energy transfer at liquid surfaces. It indeed predicts that energy transfer will increase as  $\mu$  approaches a value of one and that the maximum energy transfer will occur at that point, although in fairness it should be noted that the dynamical assumptions going into the derivation of the kinematic equation begin to fail when the mass ratio exceeds unity. We also have shown that it is capable of producing results that agree quantitatively with those deriving from simulation.

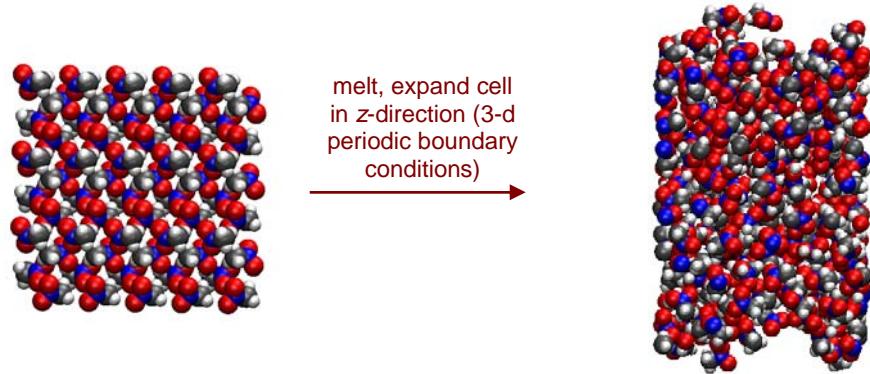
Where the kinematic model devised for gas-solid inelastic scattering misses the mark in describing gas-liquid energy transfer is in its prediction of the surface temperature dependence. For high incident energies (the case relevant to the data depicted thus far), the surface temperature correction appearing in the final factor of the kinematic equation becomes negligible, and yet we find a distinctly non-negligible dependence of trapping on the liquid temperature. An examination of the average local density of the simulated lamella as a function of distance along the axis of the simulation cell that lies perpendicular to the average surface planes makes it clear that the liquid surface roughens substantially with increasing temperature. Not only does the width of the surface region increase, but the position of the Gibbs surface advances farther from the center of the lamella. Thus, at the higher temperatures, an incident particle is more likely to be scattered inelastically away from the specular direction, more likely to experience multiple collisions with surface species, and more likely (due to an increase in the vapor pressure of the liquid) to encounter other gas atoms in the near-surface region, either before or after collision with surface atoms. With an increase in the average number of collisions between the incident and surface atoms, one anticipates that the incident atoms will lose their memory of the initial collision conditions and that trapping therefore will be less sensitive to factors such as the depth of the interaction well or the mass ratio of the collision partners. This expected behavior is precisely what we see in our simulations.



Not only does the width of the surface region increase, but the position of the Gibbs surface advances farther from the center of the lamella. Thus, at the higher temperatures, an incident particle is more likely to be scattered inelastically away from the specular direction, more likely to experience multiple collisions with surface species, and more likely (due to an increase in the vapor pressure of the liquid) to encounter other gas atoms in the near-surface region, either before or after collision with surface atoms. With an increase in the average number of collisions between the incident and surface atoms, one anticipates that the incident atoms will lose their memory of the initial collision conditions and that trapping therefore will be less sensitive to factors such as the depth of the interaction well or the mass ratio of the collision partners. This expected behavior is precisely what we see in our simulations.

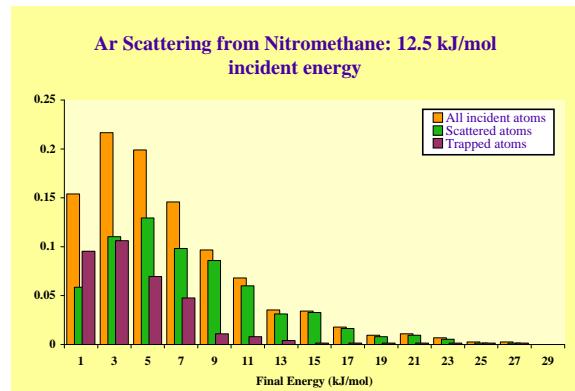
Having established that for a simple model system, kinematics and temperature-dependent surface roughening largely govern the observed energy transfer, we shifted our focus to molecular liquids, specifically to nitromethane. Initialization of the system was performed in

the same way as for the Lennard-Jones atomic liquid, with the assumed potential energy function for nitromethane being that described by Sorescu, Rice, and Thompson.



From the average number density of nitromethane molecules in our simulation cell following the creation of the free surfaces and subsequent equilibration, we can easily determine the equilibrium vapor pressure above the liquid. The value obtained at 360 K, which is 0.62 bar, agrees well with the value (0.66 bar) estimated from literature values for the enthalpy of vaporization. Although the potential function adopted for nitromethane was optimized to describe the crystalline phase accurately, that function clearly is providing a very reasonable description of our liquid-vapor equilibrium as well.

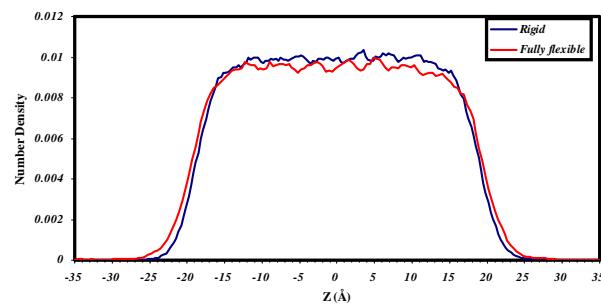
We take the impinging atoms (with masses taken to be that of argon) to be incident with a kinetic energy of  $4.2RT_{\ell}$ . With this initial energy, 35% of the atoms become trapped at the surface of the liquid—the trapping fraction here is essentially the same as that obtained in the Lennard-Jones case for the equivalent mass ratio and surface roughness—but even those that are not trapped are well on their way to becoming thermalized with the surface. The distribution of scattered atom energies shown in the figure to the right translates into a thermal accommodation coefficient of 0.81, which is very similar in magnitude to the values calculated in the case of the simple atomic liquid described previously.



It has also proven useful to examine a simplified model of nitromethane, consisting of structureless methyl and nitro groups bound by the same Morse potential used to describe the carbon-nitrogen bond in the full nitromethane molecule. Our initial interest in this diatomic model stemmed from wondering whether we could collisionally induce a decomposition reaction at a liquid surface. (Given the paucity of full reactive potential functions that describe dissociation to the correct structurally relaxed products, we believe that the diatomic model system at least provides a test of whether dissociation might be feasible under realistic deflagration conditions.) However, even for initial incident energies well in excess of the C–N bond energy, no evidence of dissociation was observed. This result suggests that energy transferred to translation or rotation of the surface species is rapidly lost to the bulk and that the probability that the surface species will undergo a collision that leads to direct excitation of the diatomic above its bond dissociation threshold is very low. Nonetheless, energy transfer from

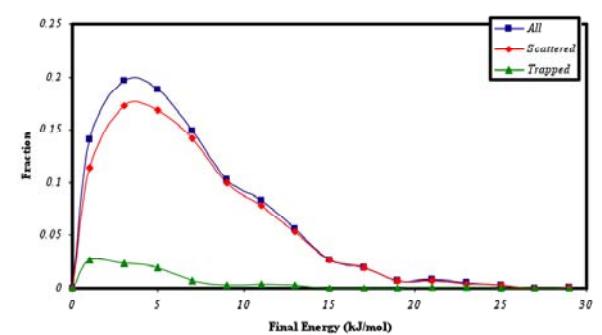
the incident atoms to the surface in this case is quite efficient. Whether we take the attraction between the incident atom and the diatomic to be strong or absent entirely, we find that the thermal accommodation coefficient is greater than 0.60. Certainly, the fraction of the initially incident atoms being trapped by the surface changes as that attraction is varied, but in all cases the majority of the incident kinetic energy is deposited in the surface.

To understand our results for the full nitromethane simulation, we again fall back on the kinematic model that described the Lennard-Jones system so well. It is not quite as easy to know how to evaluate some of the constants appearing in the equation for the fractional energy transfer in this case. The second factor in the equation, which accounts for collisions that are “off-center” clearly is problematic when the target is a molecule, and the final factor, which includes the attractive well depth, does not account for the differences in the interactions when various sites on the nitromethane are hit. If, however, we estimate the angular factor to be approximately unity on average for normal atom incidence and if we assume that the attractive well depth is negligible, then the equation predicts a fractional energy transfer at 360 K of 0.50, which agrees very well with the value of 0.52 that we obtain from a final energy analysis of the scattered atoms. If we compare the results obtained for an incident energy about seven times higher, corresponding to the incident energy used in the Lennard-Jones system simulations, then both the kinematic equation and our simulations predict a fractional energy transfer of 0.89. These recent results thus suggest that the most straightforward way of grafting detailed molecular information onto extant continuum combustion models would be to focus just on the kinematics, that the mass ratios and simple energetic corrections to the collision events capture the essentials of the dynamics.



nitromethane molecules play at most a minor role in the collisional energy transfer. To investigate this issue, we conducted a series of simulations in which the nitromethane molecules were “frozen” at their equilibrium geometries. (The SHAKE algorithm was applied in order to constrain the molecular motion.) The density profile of the lamella stemming from this constrained system is shown in the plot below along with the corresponding profile of the unconstrained, “flexible” liquid. We found very little statistical difference between the two profiles, certainly not enough to invalidate a comparison of the energy transfer in the two systems. The distribution of final argon atom energies in the rigid-nitromethane case is shown below. Qualitatively, there is very little

For larger molecules of interest as energetic materials, we recognize that we need to consider the possibility of energy transfer to the internal vibrational degrees of freedom of these molecules by direct collision rather than by general heating of the liquid. Given the role of kinematics in the energy transfer, however, we speculated that the vibrational degrees of freedom of the

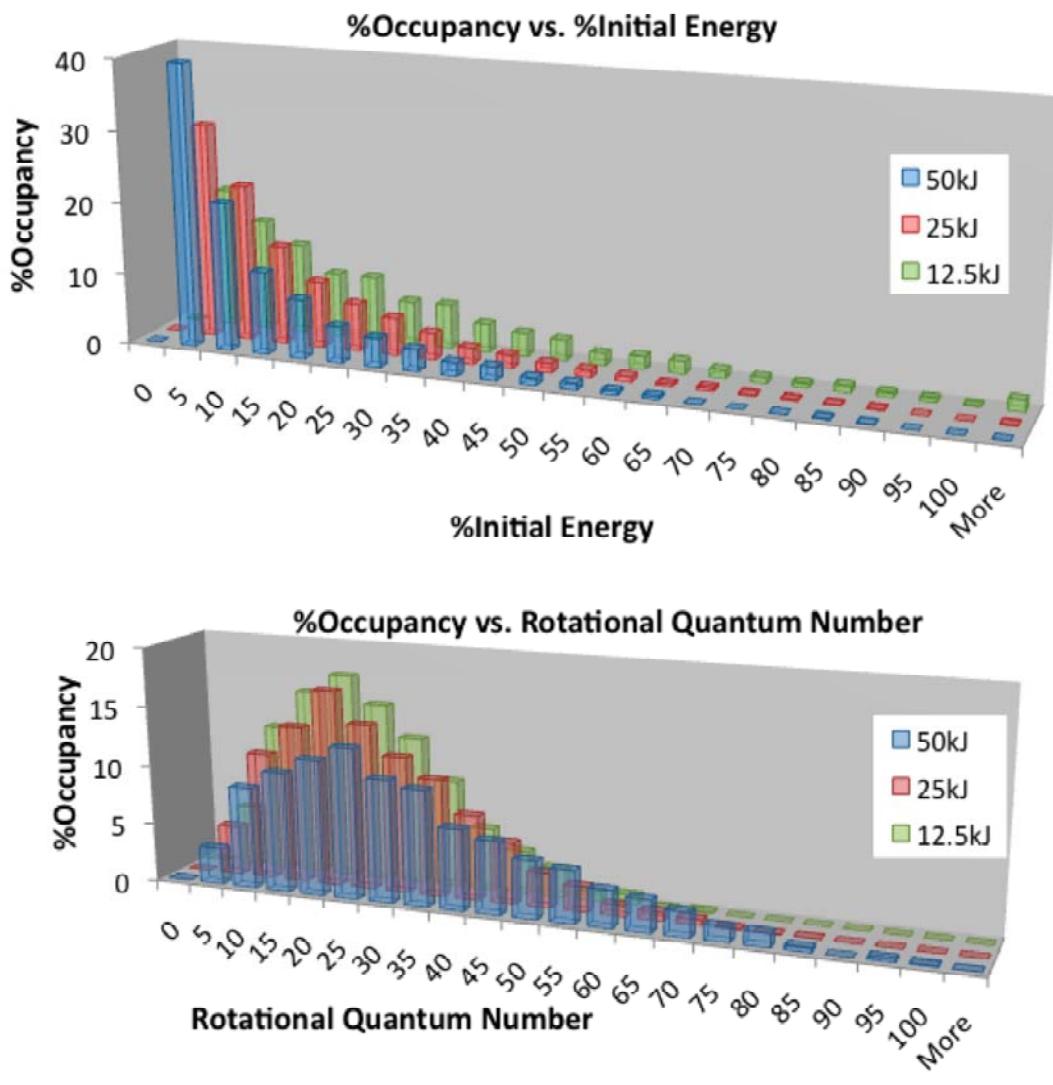


difference between the distribution of scattered atom energies shown here and the distribution obtained using the fully flexible nitromethane force field. We find a somewhat greater propensity for trapping in the rigid system that perhaps stems from the absence of a channel for feedback of energy from excited vibrational modes of the surface molecules to the argon atoms. Nonetheless, energy transfer remains efficient in this system. The estimated thermal accommodation coefficient in the rigid-nitromethane case is 0.89, which is within 10% of the value obtained when using the flexible-nitromethane model. That the surface appears to be somewhat “stiffer” when the nitromethane molecules are held rigid is also consistent with a small preference for forward scattering of the argon atoms, whereas the distribution of scattering angles is essentially symmetric in the forward and backwards directions when the rigidity criterion is relaxed. Overall, however, we conclude that internal vibrational degrees of freedom play a negligible role in the net gas-surface energy transfer at a liquid nitromethane surface.

Finally, we have extended our studies of collisional energy transfer between hot gas atoms and atomic and molecular liquid surfaces by considering the collisions of simple molecular species with a prototypical atomic liquid surface. In our previous work the role that rotational excitation of the impinging species might play in a general gas-surface collision event was left undetermined. To examine this last process, we are simulating collisions of rigid CO<sub>2</sub> molecules with a Lennard-Jones atomic liquid. These incident molecules, while translationally “hot”, are taken to be nonrotating initially. Thus, any rotational energy present in the reflected species thus is necessarily attributable to the collision event.

In the upper panel of the figure shown below, we display distributions of the final rotational energies (given as a fraction of the initial kinetic energy) of scattered CO<sub>2</sub> molecules, each corresponding to a different incident-molecule kinetic energy. Note that each of these distributions indicate that a substantial fraction of the incident energy ultimately is deposited in the rotational degrees of freedom of the scattered species, with this energy disposition mechanism becoming increasingly important as the incident energy approaches the average thermal energy of the liquid surface. Lower incident energies, of course, yield proportionally lower average energy transfer just because the energy gap between the initial incident energy and the average thermal energy of the surface is smaller. Nonetheless, higher rotational excitations are obtained when the incident energy is increased. The final rotational quantum number distributions corresponding to these energy distributions are shown in the lower panel of the figure below. Previous experimental work by Nesbitt and co-workers yielded comparable rotational excitations for CO<sub>2</sub> scattering from a high molecular weight molecular liquid, thus our work to date suggests that rotational excitation due to collisions with a nonpolar liquid surface may be only weakly dependent on the nature of the liquid species.

This project is ongoing, with an investigation of the dependence of the rotational excitation on the moment of inertia of the incident molecules currently in progress, as is a study of the incident angle dependence of the translation-to-rotation energy transfer. Our focus here remains on a full characterization of the collision dynamics in a prototypical system rather than on reproducing the results of a particular experiment inasmuch as our experience to date has indicated that the gross features of energy transfer in gas-liquid collisions are interpretable in terms of simple kinematic models.



### Scientific progress and accomplishments

1. For both atomic and molecular liquids, gas-surface energy transfer is dominated by kinematic effects. Indeed, the gross features of the energy transfer obey the dependence on masses (in particular, the ratio of the impinging species mass to the mass of the liquid species) proposed by Baule to describe energy transfer at a solid surface.
2. Energy transfer to a molecular liquid is efficient even when trapping is not.
3. In the case of liquid nitromethane, the vibrational degrees of freedom of the nitromethane molecules a negligible role in the transfer of energy due to collisions (i.e., the thermal accommodation coefficient differs by no more than 10% when vibrational degrees of freedom are “frozen”.)
4. For a molecular impinging gas, collision with the liquid surface leads to substantial rotational excitation of the species reflected from the surface. Initial results suggest that the rotational excitation may be only weakly dependent on the nature of the liquid surface.

## **Development of Methods for Predicting Solvation and Separation for Energetic Materials in Supercritical Fluids**

**Christopher J. Cramer, Alek V. Marenich, Adam C. Chamberlin, Casey P. Kelly, Benjamin J. Lynch, Ryan M. Olson, Jason D. Thompson, Paul Winget, and Donald G. Truhlar** (Department of Chemistry and Supercomputing Institute, University of Minnesota Minneapolis, MN 55455)

### **Statement of the Problem Studied**

Research is being carried out at the University of Minnesota on two projects. First is the development of theoretical methods that can be used to predict the solubilities of high-energy materials in various fluids. These types of methods have a variety of applications, including the development of improved methods for the safe recycling/disposal of many types of high-energy materials. Second is the development of new methods for predicting partial atomic charges for modeling the crystallization of high-energy materials as well as being one component of the solubility calculations. This research requires the development of charge models and solvation models that may be used for a wide range of applications including the modeling of crystalline materials. During the MURI grant period, we have developed broadly applicable computational methods for solvation free energies and partial atomic charges. Another important aspect of our research has been improving the capability and portability of charge-model and solvation-model software and distributing these programs (including detailed instruction manuals and other related documents) to fellow MURI researchers, researchers at ARL, and to the scientific community at large. We are implementing them into easy-to-use codes that are freely available via the World Wide Web. Thus Army and MURI researchers will be able to use these models and methods to facilitate the design of practical procedures for extraction, recycling, and reusing materials.

Since the MURI project began in 2002, we have focused on extending existing continuum solvation models. Eventually it would be desirable to have a model for supercritical solvents. Our work so far has been focused on improving the performance of continuum solvation models for predicting solvation free energies because solubilities can be computed using solvation free energies and pure solute vapor pressures. Research carried out under this grant examined whether calculated solvation free energies and calculated or experimental vapor pressures could be used to make accurate predictions of solubility (J. D. Thompson, C. J. Cramer, and D. G. Truhlar, *J. Chem. Phys.* **119**, 1661 (2003)). It was shown that in most cases, doing this leads to accurate values for the solubility, even for solutes that are solids at 298 K. (The vapor pressure can be calculated using our continuum solvation models because it is related to the solvation free energy of the solute in its own pure liquid phase, or, in the case of a solid, its supercooled liquid phase. We refer to this free energy as the “self-solvation free energy.”) Our continuum solvation models (labeled as SM $x$  where  $x$  indicates the version number) separate the solvation free energy into two components: the long-range bulk electrostatic contribution arising from a self-consistent reaction field treatment using the generalized Born approximation for electrostatics is augmented by the non-electrostatic contribution arising from short-range interactions between the solute and solvent molecules in the first solvation shell. Our continuum solvation models (i.e., solvation models for ordinary liquid solvents) utilize the generalized Born (GB) model in a self-consistent reaction field step to account for long-range electrostatic effects. Note that the GB model represents the solute as a collection of atom-centered spheres and atom-centered point charges. Our model also accounts for solvation phenomena beyond

electrostatics, including cavitation, dispersion, hydrogen bonding, and structural changes taking place in the first solvation shell(s), as well as local changes in the permittivity of the solvent, by modeling these effects as being proportional to the solvent-accessible surface areas (SASAs) of the atoms in the solute. The constants of proportionality are called atomic surface tension coefficients. They contain parameters (called atomic surface tension parameters) that are optimized against a training set of experimentally known free energies of solvation in water and organic solvents and that depend on a set of experimental solvent descriptors of the solvent.

### **Progress for May 2002 - August 2008 (Summary of the Most Important Results)**

#### **Improved Charge Models**

Throughout the MURI project we have been continually developing and improving our charge models, charge model 3 (CM3) and charge model 4 (CM4), that provide accurate and reliable charges to use in the GB model. CM4 is a mapping from Class II charges such as Löwdin (LPA) or redistributed Löwdin (RLPA) for diffuse basis sets that is necessary in order to correct for systematic errors in electronic population analysis techniques for charge-dependent observables. Additionally it is known that Löwdin charges are not stable for diffuse basis sets, and because diffuse functions may be important for an even-handed description of conformational energies and of negative functional groups found in many of the compounds of interest, we developed a new population analysis method, called redistributed Löwdin population analysis (RLPA). While Redistributed LPA charges are stable for diffuse basis sets, they still suffer from systematic errors similar to those found in Löwdin charges for non-diffuse basis sets. So it is necessary to map partial atomic charges obtained from either method to charges which reproduce experimentally verifiable properties such as dipole moments. We created a series of improved charge models ending with charge model 4 (CM4). CM4 uses a semiempirical charge-mapping scheme that is a function of the Mayer bond orders in the molecule. The CM4 charge model has several improvements over prior class IV charge models developed in our research group. In particular, the CM4 parameters were optimized against a larger and more diverse training set than earlier charge models. Second, when diffuse basis functions are used, CM4 maps RLPA charges rather than Löwdin population analysis charges. In addition, the CM4 parameters were chosen so that the resulting charges are not as sensitive to variations observed in the Mayer bond order when diffuse basis functions are included in the basis set. Lastly the C-H polarity was carefully developed using a specialized set of 19 different compounds designed to constrain the C-H bond polarity to physical reasonable values. An additional model was CM4M was also created. While both CM3 and CM4 were designed in such a fashion as to reliably reproduce experimental dipole moments independent of the level of theory, CM4M was designed to best reproduce experiment for a specific class of DFT functionals namely the M06 series. This allows our charge model to take full advantage of a very reliable and accurate level of theory.

#### **Validation of Charge Models**

Our development of the charge models entailed the careful validation of the model for predicting accurate charge distributions of high-energy materials (HEMs) and compounds analogous to them. The charge model 4 parameters have been optimized against a training set of dipole moment data, and validated against quadrupole moments computed at a converged level of theory. The training set is composed of 416 compounds containing many different types of functional groups that one encounters in organic chemistry. We have also shown that atomic charges calculated with CM4 yield polarization free energies (computed from the GB model) for the condensed phase that are less sensitive to the level of treatment of electron correlation than those given by other methods. This invariance to the level of treatment of electron correlation

demonstrated by the CM4 model has been critical in the development of accurate theoretical methods for modeling the solid-state condensation and dissolution of HEMs. CM4 is an improvement upon CM3, which we showed accurately reproduces the dipole moments of HEMs. This was a concern because the functional groups found in HEMs are either under-represented with respect to other functional groups present in the training set (nitro compounds) or not represented at all (nitramines, for example) in the CM3 training set. To determine whether or not the CM3 parameters are applicable for predicting accurate charge distributions of HEMs, we assembled a test set of compounds, including nitramide, dimethylnitramine (DMNA), 1,3,3-trinitroazetidine (TNAZ), 1,3,5-trinitro-s-triazine (RDX), and hexanitrohexaazaisowurtzitane (HNIW), and compared the dipole moments for different conformations of these compounds (14 in all) calculated using CM3 charges to high-level theoretical density dipole moments. Note that a density dipole moment is calculated from the one-electron density as an expectation value of the dipole moment operator, and density dipole calculations do not provide the partial atomic charges needed for condensed-phase modeling. These tests have shown that partial atomic charges from CM3 can be used to predict dipole moments for these types of compounds with similar or better accuracy as for compounds in the CM3 training set. Furthermore, this good agreement is obtained even when relatively inexpensive wave functions are used for the solute, which is important for larger solutes like HNIW.

Since publishing the results summarized above, we have been in close contact with Betsy Rice, who has begun work that involves testing whether CM $x$  (where  $x$  may be either 3 or 4) partial atomic charges calculated in the gas-phase can be used in molecular packing calculations for various high-energy materials. Some initial calculations that use CM3 gas-phase partial atomic charges with the WMIN lattice minimization program have yielded encouraging results.

### Improved Solvation Models for Room Temperature

The accurate reproduction of the free energy of solvation depends upon two factors, reproducing the electrostatic properties of the solute and reproducing the behavior of the solvent. The CM $x$  models address the first factor however the latter must also be addressed. To this end we have carefully developed a series of solvation models, solvation model 5.43R (SM5.43R), solvation model 6 (SM6), and solvation model 8 (SM8), wherein we have explored a number means to improve the accuracy of the model with the ultimate goal of making our model applicable to a broad range of solutes, including ions, and solvents. In particular we explored the importance of including explicit water molecules near highly charged sites on the solute, during the development of solvation model 6. Additionally we explored the effect of the Coulombic radii upon the solvation of ions in nonaqueous solvents during the development of solvation model 8.

The SM8 model improves upon earlier SM $x$  universal solvation models by including free energies of solvation of ions in nonaqueous media in the parametrization. SM8 is applicable to any charged or uncharged solute composed of H, C, N, O, F, Si, P, S, Cl, and/or Br in any solvent or liquid medium for which a few key descriptors are known, in particular dielectric constant, refractive index, bulk surface tension, and acidity and basicity parameters. It does not require the user to assign molecular-mechanics types to an atom or group; all parameters are unique and continuous functions of geometry. It may be used with any level of electronic structure theory as long as accurate partial charges can be computed for that level of theory; we recommend using it with self-consistently polarized Charge Model 4. The radii used for aqueous solution are the same as the ones developed previously for the SM6 aqueous solvation model, and the radii for nonaqueous solution vary as a function of the hydrogen bond acidity of the

solvent. The non-electrostatic terms are proportional to the solvent-accessible surface areas of the atoms of the solute.

### Validation of Solvation Models for Room Temperature

These models were then carefully optimized. During the course of our work we gradually improved and expanded our database the Coulomb radii in organic solvents were parameterized using a training set of 220 bare ions and 21 clustered ions in acetonitrile, methanol, and dimethyl sulfoxides, and the radii in aqueous solution were optimized using 112 ionic solutes, and 31 ion-water clusters. The non-bulk electrostatic terms were optimized against solvation free energies for a training set of 2346 solvation free energies for 318 neutral solutes in 90 nonaqueous solvents and water and 143 transfer free energies for 93 neutral solutes between water and 15 organic solvents. The model was tested with three density functionals and with four basis sets: 6-31+G(d,p), 6-31+G(d), 6-31G(d), and MIDI!6D. The SM8 model achieves mean unsigned errors of 0.5–0.8 kcal/mol in the solvation free energies of tested neutrals and mean unsigned errors of 2.2–7.0 kcal/mol for ions. The model outperforms the earlier SM5.43R universal solvation models as well as the default Polarizable Continuum Model (PCM) implemented in *Gaussian 98/03*, the conductor-like PCM as implemented in *GAMESS*, *Jaguar*'s continuum model based on numerical solution of the Poisson equation, and the GCOSMO model implemented in *NWChem*.

### Accounting for Temperature Dependence

Extraction procedures that use supercritical solvents are carried out at non-ambient temperatures and pressures. In fact, the ability to tune the properties of supercritical solvents by varying the temperature and pressure is one of their key advantages. Thus it is necessary to extend SM8 to temperatures other than 298 K in order to carry out the proposed research. During the grant period we developed a series of models for calculating aqueous solvation free energies as a function of temperature. Solvation model 6 with temperature dependence (SM6T) used the SM6 for the computation of the free energy of solvation at room temperature. Since the time when SM6T was created we developed SM8. The aqueous version of SM8 is almost identical to the aqueous SM6 model, and it has the same Coulomb radii for aqueous solution. Thus the SM6T parameters work equally well with SM8 as with SM6. Therefore the extension presented here is made using SM8 rather than SM6. We refer to the new model as SM8T.

### Validation of Model for Temperature Dependence

An important step that is necessary in order to develop SM8T is the creation of databases containing accurate experimental data for a diverse set of molecules. To optimize the parameters in SM6T, we used a database of aqueous solvation free energies for solutes containing at most the elements H, C, N, O, F, S, Cl, and/or Br (a total of 4403 solvation free energy data points for 348 solutes). Because the SM<sub>x</sub>T ( $x = 6$  or  $8$ ) models are the first theoretical models of their type for predicting temperature-dependent solvation free energies, the development of these models was an important step in determining the accuracy to which temperature-dependent solvation free energies can be predicted. When tested against the database described above, which includes aqueous solvation free energies in the temperature range of 273 K to 373 K (corresponding to the freezing and boiling points of pure water), SM8T achieves a root mean squared error of 0.09 kcal/mol. If one were to assume that temperature has no effect on the aqueous solvation free energy (null hypothesis), the root mean squared error would be significantly higher (0.70 kcal/mol). The partial atomic charge models developed for and used in the solvation models can also be used in studies of the crystal structure and energetics of high-energy materials.

## Method Development and Simulations of Physical Processes and Chemical Reactions in the Various Phases

Donald L. Thompson (University of Missouri – Columbia)

The focus of the research at the University of Missouri was on practical methods for simulations and rate calculations of physical and chemical processes in the gas, liquid, and solid phases of energetic materials; more specifically:

- Development of accurate methods for simulating melting and predicting melting points of organic solids.
- Development practical methods for computing reaction rates of reactions in condensed phases.
- Development of methods for fitting *ab initio* potential energy surfaces and for performing direct dynamics simulations.
- Using quantum chemistry methods to determine the reaction pathways for unimolecular and bimolecular reactions of energetic molecules.

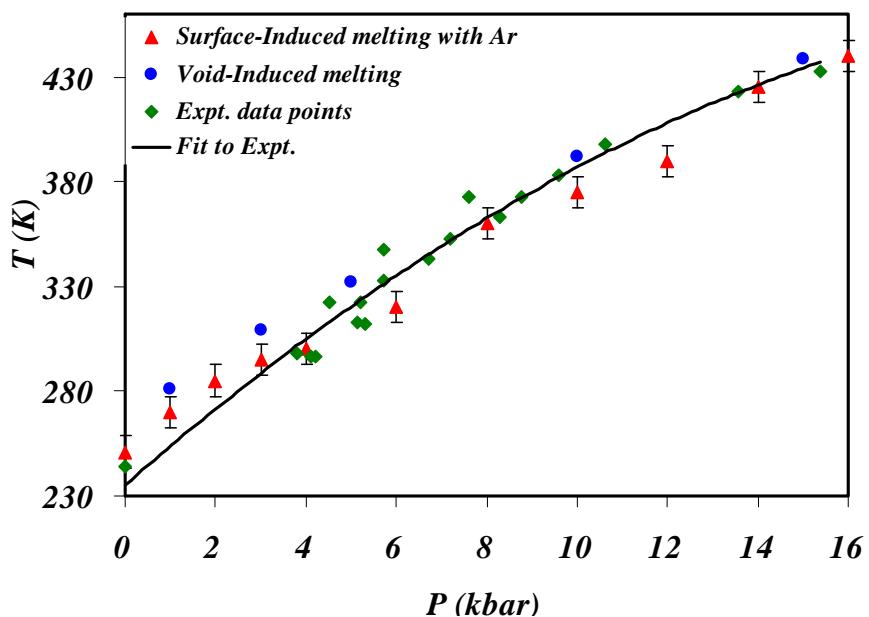
### Melting of Energetic Materials

A significant result of our work is the development and demonstration of methods for simulating solid-to-liquid phase transitions in energetic materials to predict their melting points. Prior to this grant, working with Drs. Betsy M. Rice (ARL) and Dan C. Sorescu (Okla. St. U.), we developed crystal models for organic materials that accurately describe a wide range of energetic materials. In the current grant we have used these models in studies of melting transitions of energetic materials. The simulation of melting and the prediction of melting points have been considered difficult problems. The difficulty stems from the free energy barrier for the formation of a liquid-solid interface; which can cause superheating in a perfect crystal and thus an overestimation of the melting point of the real material. We have investigated various ways of performing the simulations to determine the most practical one for use in studies of energetic materials. Prior to our work, the simulations had been restricted to atomic solids such as rare gases and metals. We first carried out a series of calculations for argon to test methods, and then we extended the studies to energetic crystals.

The introduction of vacancies in a crystal eliminates the free energy barrier that causes superheating in a perfect crystal. Alternatively, the simulations can be initiated with the solid in contact with liquid. Molecular dynamics studies of melting of nitromethane using the intermolecular interaction potential of Sorescu *et al.* (SRT) [D. C. Sorescu, B. M. Rice, and D. L. Thompson, *J. Phys. Chem. B* **104**, 8406 (2000)] have been carried out by two methods: (1) void-nucleated melting with the gradual heating of the lattice and (2) equilibration of coexisting liquid and solid phases. The results are in near agreement with each other; the small difference is attributed to the hysteresis effect associated with the direct heating process. The computed values of the melting temperature are in good agreement with the experimental data at various values of pressure ranging from 1 atm to 30 kbar. Since the void-induced melting approach is much easier to use, we have adopted it as the practical approach for predicting melting points of energetic materials. Following this work, which used our well-tested force field for nitromethane, we extended the studies to practical energetic materials, which provide critical tests of the models and simulation methods. We find that the results are sensitive to details of the potential and that for large, complex molecules the simulations are somewhat more demanding; however, the results show that approaches that we are using will be effective and

practical for predicting melting points. This work was done in collaboration with Dr. Betsy Rice at ARL.

We have developed methods for simulations of the melting transitions in perfect and imperfect crystals of energetic solids. The focus was on developing and testing methods, and thus most of the simulations were performed for nitromethane because of its relatively simple molecular structure and the availability of the accurate SRT force field;[D. C. Sorescu, B. M. Rice, & D. L. Thompson, *J. Phys. Chem. B* **104**, 8406 (2000).] however, studies of dimethylnitramine (DMNA), trinitroazetidine (TNAZ), and hexahydro-1,3,5-trinitro-1,3,5-s-triazine (RDX) were carried out. We have shown that these methods can be used to accurately predict the thermodynamic melting point and superheating temperatures, and we have used them to investigate the molecular-level details of the melting transitions in these materials. This is important in the development of realistic models of the chemistry energetic materials because phase transitions, particularly melting, are precursory to chemical initiation. Thus, our studies not only validate the force field models but also provide physical insights into the changes that occur when energetic materials are subjected to heat or pressure. An illustration of the accuracy of the methods is given in the following figure, which shows the computed and measured melting points of nitromethane as functions of pressure.



The blue circles show the results for melting initiated at voids within the crystal [P. M. Agrawal, B. M. Rice, & D. L. Thompson, *J. Chem. Phys.* **119**, 9617 (2003).] and the red triangles are the computed melting points for the crystal in contact with Ar gas [A. Siavosh-Haghghi and D. L. Thompson, manuscript in preparation.]. The experimental results [G. J. Piermarini, S. Block, & P. J. Miller, *J. Phys. Chem.* **93**, 457 (1989) & W. M. Jones & W. F. Giauque, *J. Am. Chem. Soc.* **69**, 983 (1947).] are represented by the green diamonds; the solid curve is a least-squares fit to experimental values.

## Practical Rate Calculation Methods

While the main thrust of the work has been explicit MD simulations of processes in condensed phase energetic materials, we also began development of methods for accurate rate calculations that complement the results of simulations, especially methods that can be used to either save computer time or to treat reactions that cannot be dealt with in a simulation. Specifically, we focused on methods for computing rates in the liquid phase for the initial efforts to arrive at methods for all condensed phases. In our initial effort, we used relatively simple reactions and performed the studies for reactions in simple solvents; however, the approach can be extended to more complex systems of practical interests in energetic materials research.

The solvent effects on rates of chemical reactions have been extensively studied over the years. Much of the theoretical work is based on stochastic methods such as the Langevin theory. These methods allow for computations of rate constants without explicit consideration of the detailed dynamics of the solvent, and are thus powerful for treating complex systems where full-dimensional dynamical calculations are too costly. For instance, in the Langevin theory, the solvent influence on the reacting particle is modeled by a random fluctuating force and a friction kernel. Although these stochastic methods are useful for qualitatively understanding reactions in condensed phases, rate constants cannot be directly obtained for a given realistic system because quantities involved in the models concerning the solvent effects are generally unknown and must be determined by examining the detailed dynamics of the system. Molecular dynamics (MD) simulations provide a useful means for realistically modeling detailed dynamics and elucidating reaction mechanisms. However, a full-dimensional MD study is computationally expensive and may not be feasible for complex systems. An alternative approach is to map the real system to a stochastic model by performing a few MD calculations to determine the fitting parameters in the model. We have explored such an approach.

The basic idea is that the reacting molecule is subjected to random collisions with a mean frequency  $\alpha$ . Between collisions, the dynamics of the molecule is governed solely by the equations of motion for the molecule itself. The effects of the solvent are modeled by random collisions. Under the strong collision assumption, the velocities of the molecule are randomized after each collision by sampling from the Boltzmann distribution while the coordinates are held fixed. Since only the motion of the molecule is explicitly treated, the method is far less costly than full-dimensional MD simulations. The parameter used to model the solvent effects is the collision frequency  $\alpha$ , which is related to the liquid density  $\rho$  of the system. There have been studies where both MD simulations and the stochastic dynamics method were employed on the same system; but no attempt, to our knowledge, had previously been made to quantitatively relate  $\alpha$  and  $\rho$  for any system.

We first investigated this idea with an application to *cis-trans* isomerization in HONO, which is one of the simplest molecules that exhibit *cis-trans* isomerization and one that has been extensively studied experimentally and theoretically.[Y. Guo and D. L. Thompson, *J. Chem. Phys.* **120**, 898 (2004).] We used a model system with a HONO molecule embedded in liquid krypton and performed MD simulations to obtain isomerization rates at several liquid densities. We also computed rate constants using the stochastic dynamics method for a wide range of collision frequencies  $\alpha$  for these two sets of computed rates. We then examine the relationship between the liquid density  $\rho$  and the collision frequency  $\alpha$ . Comparisons of the two sets of the

computed rates show that for a wide range of liquid densities there is a simple linear relation between the liquid density  $\rho$  and the collision frequency  $\alpha$ , that is,  $\alpha = c\rho$ . This suggests that once the constant  $c$  is determined from a molecular dynamics calculation at a single density, the reaction rates can be obtained from stochastic dynamics calculations for the entire range of liquid densities where  $\alpha = c\rho$  holds. The applicability of the combined molecular dynamics and stochastic dynamics approach provides a practical means for obtaining rate constants at considerable savings of computer time compared to that required by using full-dimensional molecular dynamics simulations alone. Given the success of this study, we next carried out a similar study of bond fission in HONO (i.e., HONO  $\rightarrow$  OH + NO). [Y. Guo and D. L. Thompson, *Chem. Phys. Letters* **418**, 351-354 (2006).]

Intuitively, the solvent effects on dissociation reactions should be different from those for isomerization; the cage effect due to the solvent that forces recombination should be a prominent factor in dissociation reactions. Thus, the relation between  $\alpha$  and  $\rho$  as well as the dependence of the reaction rate on  $\rho$  are expected to be different from that for isomerization. To establish the relation between  $\alpha$  and  $\rho$ , we have performed two sets of calculations. We calculated the rate as a function of  $\alpha$  using the stochastic dynamics method. We also calculated the rate at four liquid densities by using the full-dimensional MD simulations with a HONO molecule inside liquid Kr. The relation between  $\alpha$  and  $\rho$  was found by pairing  $\alpha$  and  $\rho$  that have the same rate. In our study of the *cis-trans* isomerization of HONO in liquid Kr, we found that  $\alpha$  and  $\rho$  obey a simple linear relation,  $\alpha = c\rho$ . For the O-N bond dissociation of HONO in liquid Kr, we found that the relationship is more complicated, but is accurately described by an analytical expression. We have also found that the solvent effects are different for the isomerization and dissociation reactions. For isomerization the rate is in the low-collision regime and increases with increasing liquid density, whereas for dissociation the rate is in the high-collision regime and decreases with increasing liquid density.

In both cases, based on one MD simulation at a single density, the reaction rates can be obtained from stochastic dynamics for a wide range of liquid densities. The approach thus provides tremendous savings of computational time compared to full-dimensional MD simulations. Future work should be carried out to extend the studies to larger, more complicated systems, including more realistic energetic molecules and in reactions in neat liquids.

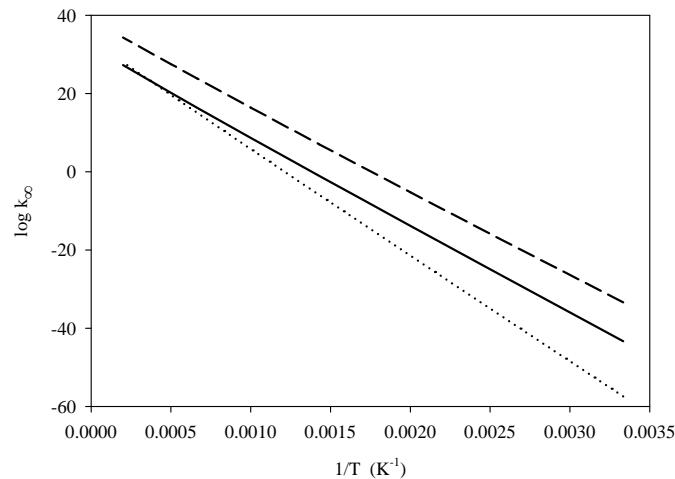
### Reaction Pathways for Unimolecular Dissociations of Energetic Molecules

A major challenge to theoretical chemists and a particular need in energetic materials research is the development of methods for simulations and rate calculations for sequential, branching reactions. The practical problems range from soot formation to the decomposition of an energetic material such as RDX. We have pursued two lines of research on this problem. First, we used quantum chemistry to explore the transition states and intermediates in the chemical decomposition of energetic molecules. The other focused on methods for fitting *ab initio* potential energy surfaces and for performing direct dynamics simulations. Quantum chemistry studies of the decomposition pathways of 1,3,3-trinitroazetidine (TNAZ) [S. Alavi, L. M. Reilly, and D. L. Thompson, *J. Chem. Phys.* **119**, 8297 (2003).] and dimethylnitramine [G. F. Velardez, S. Alavi, and D. L. Thompson, *J. Chem. Phys.* **123**, 074313 (2005).] have been carried out. Possible decomposition transition-states, intermediates, and products of TNAZ were identified and the structures, energies, and vibrational frequencies were determined at the B3LYP/6-31G(*d,p*) level. Four major pathways are apparent. Two pathways are initiated by the

fission of the N-NO<sub>2</sub> and C-NO<sub>2</sub> bonds to yield radical intermediates, while the other two pathways involve the molecular elimination of HONO. Energy profiles for the pathways and possible routes to some of the experimentally observed species of TNAZ decomposition have been determined. The energies required to initiate the NO<sub>2</sub> bond fission pathways are 4 to 8 kcal/mol lower than the HONO elimination pathways. In the gas phase, the NO<sub>2</sub> elimination pathways will be the dominant routes for TNAZ decomposition. In the condensed phase, however, this trend may be reversed.

Examination of the reported experimental and theoretical results from several researchers shows that there is an significant dispersion in the values of the Arrhenius parameters of the rate constants for the unimolecular decomposition of DMNA. The structures and energies of the reactant, intermediates, products, and transition states of the initial stages of DMNA decomposition of have been determined by quantum chemical calculations at several levels of theory. Kinetic parameters for these decomposition steps have been obtained using the RRKM formalism for the range 300-5000 K. The pathways considered are NO<sub>2</sub> elimination, HONO elimination, and NNO<sub>2</sub>-NONO rearrangement. The NO<sub>2</sub> elimination channel is the main channel of gas phase decomposition of DMNA in the 300-5000 K range of temperatures. The HONO elimination channel has the next lowest decomposition energy but at high temperatures the nitro-nitrite rearrangement competes with it.

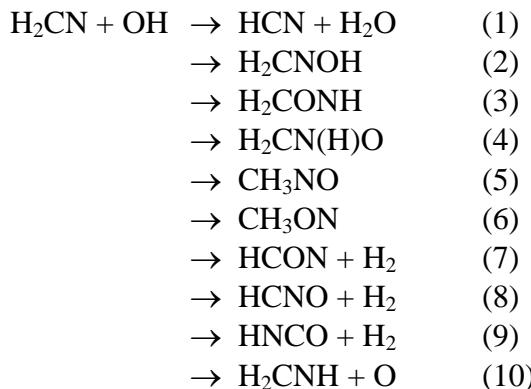
The rate constants as functions of temperature for NO<sub>2</sub> elimination, HONO elimination, and nitro-nitrite arrangement have been obtained from values of the energies and frequencies using RRKM theory; Arrhenius plots are shown in the figure below, where the curves are identified as follows: (---) NO<sub>2</sub> elimination, (—) HONO elimination, and (….) nitro-nitrite rearrangement.



The Arrhenius parameters for NO<sub>2</sub> elimination are in good agreement with the values of previous theoretical studies. The HONO elimination channel has a lower value of the pre-exponential factor compared to NO<sub>2</sub> elimination because the transition state for the HONO elimination pathway is entropically unfavorable. Clearly, the NO<sub>2</sub> elimination is the main decomposition channel of DMNA in the range of 300-5000 K. The HONO elimination has a higher rate than the nitro-to-nitrite rearrangement but at high temperatures the rates of these two reactions becomes comparable. The experimental evidence is that the presence of NO in the

DMNA decomposition products is due to the nitro-nitrite rearrangement followed by breaking of the weak NO-NO bond. Our results show that at low temperatures, this channel is the third in importance and becomes comparable with the HONO elimination channel only at higher temperatures.

We carried out quantum chemistry computations to investigate the reactions of the radicals produced in the decomposition of cyclic nitramines.[Methylene amidogen H<sub>2</sub>CN is an intermediate in the thermal decomposition of HDX and RDX and in a number of other chemical processes.[G. F. Adams and R. W. Shaw, Jr. *Annu. Rev. Phys. Chem.* 1992, **43**, 311.] Recently, Nizamov and Dagdigian [B. Nizamov and P. J. Dagdigian, *J. Phys. Chem. A* 2003, **107**, 2256.] studied room-temperature chemical reactions involving H<sub>2</sub>CN and reported the room-temperature rate constant for the H<sub>2</sub>CN + OH reaction. Their results indicate that the hydrogen abstraction channel to form HCN + H<sub>2</sub>O is the predominant reaction channel. We performed high-level *ab initio* calculations to identify the likely products of the ground state reaction between H<sub>2</sub>CN and OH, with the eventual goal of evaluating rate constants for these reactions. The reaction channels considered are:



All possible isomeric forms of each product were investigated. With the exception of HCN, H<sub>2</sub>O, and H<sub>2</sub>, both singlet and triplet states were examined for the molecular products. We have determined transition states and for transformations between the possible products.

### More Efficient use of *Ab Initio* Potential Energy Surfaces

An important part of predicting the behavior of energetic materials is better practical methods for computing the rates of chemical reactions. A critical problem is the formulation of PESs. For purely predictive methods it necessary that the PESs be based on quantum chemistry calculations, but this remains a major obstacle to applications to large polyatomic molecules and radicals. The most straightforward way to make use of *ab initio* results is to simply compute the forces “on the fly” during a simulation; however, the difficulty here is that studies are restricted to the lower-level quantum methods, which are often not sufficiently accurate for reliable predictions of rates. The common alternative to “direct dynamics” is to fit the *ab initio* energies to an analytical function, which allows for much more rapid evaluations of the forces during simulations as well as scaling of the *ab initio* results to correct for the inaccuracies inherent in a low-level theory. Fitting a global PES is extremely tedious and not readily generalizable, thus a huge investment of human labor is required in each case. Furthermore, the analytical forms are not sufficiently flexible to accurately fit the *ab initio* points. This was our motivation for suggesting, in the 1970’s, that local fitting functions should be used to fit *ab initio* energies. We proposed using cubic splines, which provide the desired flexibility to yield accurate, smooth first and second derivatives but requires a fairly dense grid of *ab initio* points.[ D. R. McLaughlin and

D. L. Thompson, J. Chem. Phys. **59**, 4393 (1973). The modified Shepard methods suggested by Ischtwan and Collins [J. Ischtwan and M. A. Collins, J. Chem. Phys. **100**, 8080 (1994).] in 1994 are superior to cubic splines. They have combined surface fitting with MD simulations in an iterative scheme for successively and automatically improving the PES. This procedure selects the locations for additional *ab initio* calculations in regions of configuration space that are dynamically important. The procedure is simple and readily automated but gradients and Hessians, which are not readily available in the high-level *ab initio*, are required at every point. We have developed interpolative moving least-squares (IMLS) fitting procedures that promise to be more useful than other methods, mainly because it does not require derivatives.[Y. Guo, L. B. Harding, A. F. Wagner, M. Minkoff, and D. L. Thompson, J. Chem. Phys. **126**, 104105 (2007).]

We have begun applications of the IMLS methods to reactions important in the decomposition of nitramines, specifically a study of the unimolecular decomposition of H<sub>2</sub>CN, which is currently under study in Professor Paul Dagdigian's laboratory at Johns Hopkins. *Ab initio* energies were fit and rates of dissociation computed. These results are available in advance of Professor Dagdigian's measurements of the rates, thus they will be truly predictive.

The first objective was to establish the accuracy of this approach for a significant chemical reaction. The long-term goal, which is beyond the scope of this project, is to develop software that manages the quantum chemistry calculations in direct response to the needs of a MD simulation to provide an *ab initio* prediction of a specified reaction rate. If successful, and the prospects are good, this could make MD studies of reactions a practical tool for all who are interested in reaction kinetics rather than a technique limited to use by experts.